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STRUCTURED ELECTRODE INTERFACES

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L. Blum

Physics Department, POB 23343, University of Puerto Rico,
Rio Piedras, P.R. 00931-3343, USA

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STRUCTURED ELECTRODE INTERFACES

LESSER BLUM

Department of Physics, PO Box At, University of
Puerto Rico, Rio Piedras, Puerto Rico, 00931

Abstract

A general discussion of the structure of the charged interface when the surface is not smooth is presented. In particular, the effect of a structured electrode is presented.

Introduction

The electrochemical interface offers a particularly big challenge to the scientist: because it is such an important system a lot has been worked on it, and yet because of the intrinsic technical difficulties associated with non-extra high-vacuum surface physics, very little direct structural evidence is available for the active electrode.

There is an increasing body of evidence coming from optical spectroscopy-Techniques such as Surface Enhanced Raman effect (SERS), [1] Surface Infrared spectroscopy (SIRS) [2], and more recently, second harmonic generation (SHG) [3] are fine examples of diagnostics for structural changes (changes in bonding arrangements) but do not provide unequivocal structural information: The shifts and intensities of the spectral lines depend on local field as well as local structure. — R/H

Quite interesting information can be obtained from ex-situ experiments, in which the electrodes are examined by surface sensitive techniques [4], (LEED, for example in extra high vacuum. As has happened in the science of solid surfaces, we learn that the structure of electrodes is rich and complicated. For example, there may be ordered 2-dimensional phases formed by species present at the interface. Take, for example the case of Pb deposited on silver (111). This is a case of under potential deposition. A mono layer of Pb is deposited much before bulk lead is. Kolb,[5] and co workers have performed

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ex-situ studies of this system and shown that there can be two phases of Pb. One is a dense, hexagonal phase which, however, is incommensurate with the underlying Ag(111) surface. A low density phase (1/3 of full coverage) is also observed in these experiments. At intermediate coverings a mixture of the two phases is observed.

The question is: what happens in the active electrode? It is quite fortunate that, direct, x-Ray observations can (and recently have[6] been made on this system.

The results indicate that:

- a) at high voltages (-.53 to - 1 v) only the dense phase exists.
- b) at lower voltages, (-.38, -.39 v) where the shoulder in the voltamogram is, the low density, commensurate $\sqrt{3} \times \sqrt{3} R 30^\circ$ phase is not observed.
- c) furthermore, at intermediate coverage, only the dense phase exists in the form of clusters. These clusters grow in size, (and number) shrink and twist slightly during the deposition, which takes place between -.375 and -.525 v. from x-Ray diffraction experiments[7]) .The film seems to be stable between -.53 V and -1 .V.

The question now is: how do we formulate a statistical mechanical theory of the double layer (in this case, the inner Helmholtz layer) in which the structure of the solid surfaced is included - clearly this is an old problem that has been discussed by many distinguished researchers like Frumkin, Levine, Fawcett, just to mention a few names. But their approach was necessarily more empirical than fundamental. Our point of view is going to the different. We will propose simple, schematic models of the structured interfaces, about which we can make precise statements. (It is similar to the drunkard who lost the key to his home somewhere, but looks for it under a light pole, because it is the only place where he can see). So, let us consider a smooth electrode again (one sided, meaning a hard impenetrable surface, or two sided, which consists of a surface separating two conducting media), and let us decorate it with sticky sites[8] .

$$\exp [-\beta u(r)] = 1 + \lambda \delta(r - \sigma^-)$$

where $\delta (r)$ is Dirac's delta function, β is Boltzmann's thermal factor, and λ is the sticking probability. Again we start at the light pole, like the drunkard: Our model may not be very close to the real

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interface, but it has been simplified so that we may be able to understand it. Let us now turn to an even simpler version (Jancovici[9]): In two dimensions, the one component plasma (OCP), that is, the system in which the positive ions, for example have been smeared to become a uniform neutralizing background, and the negative ions are point charges. The negative ions interact through the potential.

$$u(r_{ij}) = -e^2 \ln |r_{ij}| \quad (2)$$

For a specific temperature T , for which

$$\beta e^2 = e^2/kT = 2 \quad (3)$$

The statistical mechanics of the OCP is completely solvable. This means that we can use this model as a tool (of "experimental mathematics") to test exact sum rules, valid for the more realistic 3 dimensional models. Very briefly, to see why this model is exactly solvable, consider the configurational canonical partition function of a system of N negative charges

$$\begin{aligned} Z_N(\lambda) &= \frac{1}{N!} \int dr_1 \dots dr_N \exp [-\beta(\sum u_{ij} + v_i)] \\ &= \frac{1}{N!} \int dr_1 \dots dr_N \exp [-\beta(\sum v_i)] \exp [\beta(\sum e^2 \ln |r_{ij}|)] \\ &= \frac{1}{N!} \int dr_1 \dots dr_N \exp [-\beta(\sum v_i)] |\prod (r_i - r_j)|^2 \quad (4) \end{aligned}$$

Here, $v_i = v_i(r_i)$ is the interaction of the charge with the background. In the simplest case, it will be the uniform charge density, in which case $v_i \propto |r_i|^2$.

There seems to be another two ingredients that are necessary to obtain explicit solutions for these models[10]

a) that the product in equation (4) can be written as a determinant of dimension $N \times N$.

b) that the determinant can be diagonalized for arbitrary values of N . This diagonalization has been achieved for backgrounds which mimic one and two sided electrodes, and, in general for arbitrary forms of



$v_i(x)$ (Here $r = x, y$).

More recently it has been shown[11] that the case of a structured interface of a two dimensional OCP can be solved explicitly. In the simplest case, $v_i = x_i + V_{st}$ and V_{st} is defined

$$\exp [-\beta V_{st}(r)] = 1 + \lambda \sum_{m=1}^M \delta(y-y_m) \delta(x) \quad (5)$$

where y_m is the position of the m^{th} sticky site. All the sticky sites are located at the straight line defined by $x=0$, and the system is otherwise uniform. M is the total number of sites for a finite length L of the line.

$$\omega = M/L \quad (6)$$

is the density of the sites on the line. The excess free energy $\Delta f^e = \Delta F/L$ due to the presence of the line of adsorbing sites is then

$$\Delta F = -kT \ln \left[\frac{Z_N(\lambda)}{Z_N(0)} \right] \quad (7)$$

$$\Delta f^e = \Delta F/L = -kT \omega \int_0^1 d\zeta \ln[1 + \lambda \rho \theta_3(\zeta, t)] \quad (8)$$

where

$$t = \pi \rho / 2 \omega^2$$

ρ is the density of charges in the bulk system, and $\theta_3(\zeta, t)$ is the Jacobi theta function defined by[12]

$$\theta_3(\zeta, t) = \sum_{m=-\infty}^{\infty} e^{-tm^2 + 2\pi i m \zeta} \quad (9)$$

We can also compute other properties of this model. The fraction of occupied sites is (the adsorption isotherm!).

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$$n_a = \int_0^1 d\zeta \frac{\lambda \rho \theta_3(\zeta, t)}{[1 + \lambda \rho \theta_3(\zeta, t)]} \quad (10)$$

and the density profile $\rho(r)$ is, using

$$\rho(r) = y(r) \left[1 + \lambda \sum_{m=1}^M \delta(r - r_m) \right] \quad (11)$$

$$y(r) = \rho - \rho^2 e^{-\pi \rho |z|^2} \int_0^1 d\zeta \frac{F(\zeta, z, t)}{[1 + \lambda \rho \theta_3(\zeta, t)]} \quad (12)$$

with

$$\begin{aligned} 2F(\zeta, z, t) = & \theta_3(\zeta + t\omega z/\pi, t) \theta_3(\zeta + t\omega z^*/\pi, t) \\ & + \theta_3(\zeta - t\omega z/\pi, t) \theta_3(\zeta - t\omega z^*/\pi, t) \end{aligned} \quad (13)$$

$$\text{and } z = x + iy; z^* = x - iy. \quad (14)$$

Consider now the case of the one sided interface (a) or two sided interface (b). Both of these cases were recently discussed by Cornu [13]. We follow her analysis closely. For case (a): In that case we get

$$\Delta f^e = -kT \omega \int_{\sigma/\omega}^{1+\sigma/\omega} d\zeta \ln[1 + \lambda \rho H_1(\zeta)] \quad (15)$$

$$n_a = \int_{\sigma/\omega}^{1+\sigma/\omega} d\zeta \frac{\lambda \rho H_1(\zeta)}{[1 + \lambda \rho H_1(\zeta)]} \quad (16)$$

where

$$H_1(\zeta) = \sum_n \zeta S(\zeta + n) \quad (17)$$

$$S_1(u) = 2\sqrt{\pi}/\sqrt{t} \frac{e^{-\pi^2 u^2/t}}{1 + \Phi(\pi u/\sqrt{t})} \quad (18)$$

$$= \frac{d}{du} [1 + \Phi(\pi u \sqrt{t})]$$

$$\Phi(u) = 2/\sqrt{\pi} \int_0^u dv e^{-v^2} \quad (19)$$

and the single particle density is (regular part)

$$y(r) = \rho e^{-2\pi\rho x^2} \int_{\sigma/\omega}^{1+\sigma/\omega} d\zeta \sum_n S_1(\zeta+n) e^{2\pi\omega z(n+\zeta)} \quad (20)$$

$$\left[e^{2\pi\omega z^*(n+\zeta)} - \frac{\lambda\rho}{[1+\lambda\rho H_1(\zeta)]} \sum_m S_1(\zeta+m) e^{2\pi\omega z^*(m+\zeta)} \right]$$

For the double-sided model of the interface (b) we have

Excess free energy

$$\Delta f^s = -kT \omega \int_0^1 d\zeta \ln \left[1 + \lambda\rho_a H_2(\zeta) e^{-2(\mu_a - \mu_b)} \right] \quad (21)$$

Adsorption isotherm (fraction of occupied sites)

$$n_a = \int_0^1 d\zeta \frac{\lambda\rho_a H_2(\zeta) e^{-2(\mu_a - \mu_b)}}{\left[1 + \lambda\rho_a H_2(\zeta) e^{-2(\mu_a - \mu_b)} \right]} \quad (22)$$

Single particle density

$$y(r) = \rho_a e^{-2\pi\rho_a x^2} e^{-2(\mu_a - \mu_b)} \int_0^1 d\zeta \sum_n S_2(\zeta+n) e^{2\pi\omega_z(n+\zeta)} \quad (23)$$

$$\left[e^{2\pi\omega_z^*(n+\zeta)} - \frac{\lambda\rho_a H_2(\zeta) e^{-2(\mu_a - \mu_b)}}{\left[1 + \lambda\rho_a H_2(\zeta) e^{-2(\mu_a - \mu_b)} \right]} \sum_m S_2(\zeta+m) e^{2\pi\omega_z^*(m+\zeta)} \right]$$

where

$$H_2(\zeta) = \sum_n S_2(\zeta+n) \quad (24)$$

$$S_2(u) = 2\sqrt{\pi}/\sqrt{t} \frac{e^{-\pi^2 u^2/t}}{\operatorname{erfc}(-\pi u/\sqrt{t}) + m e^{-\pi^2 u^2/t} \operatorname{erfc}(m\pi u/\sqrt{t})} \quad (25)$$

with

$$\operatorname{erfc}(u) = 1 - \Phi(u) \quad (26)$$

$$m = \frac{\sqrt{\rho_a}}{\sqrt{\rho_b}} \quad (27)$$

Nest question is: can we draw conclusions from the two dimensional models that will be also valid for the three dimension case?

Consider now the case of an impermeable wall in 3d, decorated with an array of sticky sites - we use the definition

$$\rho_i(1) = y_i(1) \exp[-\beta v_i(\mathbf{r})] =$$

$$= y_i(1) \left[1 + \delta(z) \sum_{n_1, n_2} \lambda_a \delta(\mathbf{R} - n_1 \mathbf{a}_1 - n_2 \mathbf{a}_2) \right] \quad (28)$$

where $\rho_i(1)$ is the density of species i , $\mathbf{r} = (x, y, z)$, $\mathbf{R} = (y, z)$, and the sum n_1, n_2 is over all the sites on the surface. Then, we can derive a contact theorem that will relate the contact density to the charge on the wall and thermodynamic properties of the fluid [14]. Assume that the sticky sites form a regular lattice, and that the area of the unit

cell in that lattice is A. From (28), we write

$$\begin{aligned}
 -kT \vec{\nabla}_1 \rho_i(1) = & \rho_i(1) \vec{\nabla}_1 u_i(1) - y_i(1) \vec{\nabla}_1 e^{-\beta v_i(1)} \\
 & + \sum_j \int d^2 \rho_{ij}(12) \vec{\nabla}_1 u_{ij}(12)
 \end{aligned} \quad (29)$$

where $v_i(1)$ is the sticky potential (1) alone and all the other contributions to the single ion potential are included in $U_i(x_1)$ and $u_{ij}(12)$ is the two body potential. This equation is very complicated because it is three dimensional. If we now take averages over the unit cell, that is, we define

$$\bar{y}_i(0) = 1/A \int_{\text{cell}} dx_1 dy_1 \rho_i(x_1, y_1, z_s) \quad (30)$$

then we get by integration

$$kT \sum_i \bar{y}_i(0) = P_{\text{bulk}} + \epsilon/8\pi \langle E_z^2 \rangle_0 + kT\lambda \sum_i \left. \langle \partial y_i(1)/\partial z_1 \rangle \right|_{x=0} \quad (31)$$

where P_{bulk} is the bulk pressure, ϵ is the dielectric constant, $\langle E_z^2 \rangle_0$ is the mean square bare (vacuum) field at the undecorated interface.

This contact theorem is verified by the exactly solvable model

Let's then try to give a more quantitative treatment of this model[15]. We start by a model in which we have a hard sphere fluid in contact with a wall decorated with sticky sites. Let us call H_0 the hamiltonian of the N particle system without the sticky sites, and the sticky potential

$$H_s = \sum_{i=1}^N v_i(1)$$

Then

$$Z(0) = \frac{1}{N!} \int d\mathbf{r}^N e^{-\beta H_0} \quad (32)$$

$$Z(\lambda) = \frac{1}{N!} \int d\mathbf{r}^N e^{-\beta(H_0 + H_s)} \quad (33)$$

and because of (1)

$$Z(\lambda) = \frac{1}{N!} \int d\mathbf{r}^N e^{-\beta H_0} \prod_{i=1}^N \left[1 + \lambda \sum \delta(z_i) \delta(\mathbf{R} - \mathbf{R}_i) \right] \quad (34)$$

Divide and multiply by $Z(0)$, and recall the definition of the s -body distribution functions, then

$$\frac{Z(\lambda)}{Z(0)} = \sum \frac{\lambda^s}{s!} \rho_i^0(\mathbf{R}_1, \dots, \mathbf{R}_s) \quad (35)$$

with

$$\begin{aligned} \rho_i^0(\mathbf{R}_1, \dots, \mathbf{R}_s) &= \frac{1}{Z(0)N!} \int d\mathbf{r}_{s+1} \dots d\mathbf{r}_N e^{-\beta H_0} \\ &= g_s^0(\mathbf{R}_1, \dots, \mathbf{R}_s) \prod \rho_i^0(\mathbf{R}_i) \end{aligned} \quad (36)$$

where $\rho_i(r)$ is the singlet distribution function for the undecorated model. Using standard thermodynamics, and the fact that λ can be identified up to a multiplicative constant (or, equivalently up to a shift in the reference chemical potential) with the fugacity of the adsorbed particles, we get

$$\Delta F = kT \ln \left[\frac{Z(\lambda)}{Z(0)} \right] \quad (37)$$

$$\Delta f_s = \Delta F / A \quad (38)$$

$$n_s = (1/\omega A) \frac{\partial \ln Z(\lambda)}{\partial \ln \lambda} \quad (39)$$

and the Gibbs equation

$$\Delta \Gamma = \Gamma(\lambda) - \Gamma(0) - \frac{\partial \Delta f_s}{\partial \mu} \quad (40)$$

where $\Gamma(\lambda)$ is the total surface excess (decorated) and $\Gamma(0)$ the undecorated one.

Clearly starting with (35), we have formal expressions to compute the properties of the interface. However we need to know the distribution functions of the undecorated system to all orders.

We did, indeed, know this function for the 2-D, solvable model. But we do not know it in general. So we have to make approximations, the simplest of which is Kirkwood's superposition approximation which is

$$g_s^0(\mathbf{R}_1, \dots, \mathbf{R}_s) = \prod_{i,j}^s g_{ij}^0(\mathbf{R}_i, \mathbf{R}_j) \quad (41)$$

If we now introduce the potential of mean force between particles in sites, i, j of coordinates $\mathbf{r}_i = (0, \mathbf{R}_i)$, $\mathbf{r}_j = (0, \mathbf{R}_j)$

$$\omega_{ij} = -kT \ln g_{ij}(\mathbf{r}_i, \mathbf{r}_j) \quad (42)$$

Then we can rewrite (35) as

$$\frac{Z(\lambda)}{Z(0)} = \sum_{\substack{\text{All sites} \\ \text{on the surface}}} \frac{\lambda^s \prod_{i=1}^s \rho^0(\mathbf{r}_i)}{s!} \exp \left[-\beta \sum_{nn} w_2^0(\mathbf{r}_i, \mathbf{r}_j) \right] \quad (43)$$

We observe now that this is just isomorphic to the grand canonical partition function of a two dimensional lattice gas in an external field. The site-site interaction is given by the potential of mean force ω_{ij} , and the external field by a potential

$$v_i = -kT \ln \rho_i^0(0) \quad (44)$$

Using the Percus-Yevick expressions for $g_2^0(\sigma)$ and for $\rho^0(0)$

$$\begin{aligned} g_2^0(\sigma) &= (1 + \eta/2)/(1 - \eta)^2 \\ \rho^0(0) &= (1 + 2\eta)/(1 - \eta)^2 \\ \eta &= \pi/6\rho\sigma^3 \end{aligned} \quad (45)$$

we get, using mean field theory (Bragg-Williams approximation).

$$n_a = \frac{\lambda \rho_i^0(0) [g_2^0(\sigma)]^{n_a c}}{\left[1 + \lambda \rho_i^0(0) [g_2^0(\sigma)]^{n_a c} \right]} \quad (47)$$

where c is the number of nearest neighbors in the lattice. This is an equation for the fraction of occupied sites n_a . At high densities and low coupling constants there is a phase transition. The reason for this is that the contact probability $g_2^0(\sigma)$ increases with density, meaning that the effective pair attraction of particles in occupied sites also increases with density. The effect of the sticky parameter λ

(actually, of $\lambda \rho_1^0(0)$) is that of the external field, which has the effect of attracting indiscriminately to any site of the interface, and therefore has a disordering effect.

Very recently Caillol, Levesque and Weis[16], have carried out a detailed Monte Carlo simulation of a system that is similar to the sticky surface system. The major difference is that the sticky sites are not points, but rather small muffin tins (camembert boxes) of cylindrical shape. Any ways the simulation does not see a sharp transition, as predicted by the theory. However, the qualitative effect of clustering is clearly noticeable.

Furthermore, the size of the clusters increases with the coverage n_a , and furthermore, they are not really commensurate with the lattice of adsorbing sites. This is due to the fact that because of thermal rattling, the 'effective' diameter of the adsorbate is bigger than σ . Therefore the clusters are not commensurate with the surface. But certainly, this model does imitate the features of our Pb/Ag(111) interface, at least qualitatively in the sense that the effect on the higher coverage is to decrease the distance between the adsorbed particles, while the size of the clusters increases. To see a sharp transition we probably have to make the camembert boxes smaller, or even introduce an attractive potential between the adsorbed particles. This does not seem to be the case in the computer simulation, or the experimental data on the Pb/Ag(111) system.

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